

UNCLASSIFIED

MASTER COPY

FOR REPRODUCTION PURPOSES

SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS					
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.					
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S) Also 25014.8-EG					
4. PERFORMING ORGANIZATION REPORT NUMBER		7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office					
6a. NAME OF PERFORMING ORGANIZATION Yale University	6b. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211					
5c. ADDRESS (City, State, and ZIP Code) New Haven, CT 06520-2159	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAL03-87-K-0098						
3a. NAME OF FUNDING/SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL (If applicable)	10. SOURCE OF FUNDING NUMBERS					
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	<table border="1"> <tr> <td>PROGRAM ELEMENT NO.</td> <td>PROJECT NO.</td> <td>TASK NO.</td> <td>WORK UNIT ACCESSION NO.</td> </tr> </table>			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.				
11. TITLE (Include Security Classification) Improvement of Gas Analysis by Enrichment of Trace Species - Unclassified							
12. PERSONAL AUTHOR(S) John B. Fenn and Juan F. de la Mora							
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 9/21/87 TO 5/30/90	14. DATE OF REPORT (Year, Month, Day) 1990, Sept., 30	15. PAGE COUNT 8				
16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.							
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)					
FIELD	GROUP	SUB-GROUP					
		trace gas analysis, aero dynamic enrichment, particle focusing, electrospray, aerosols, mass spectrometry, inertial separation.					
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The objective was to develop a continuous on-line method for enhancing the sensitivity of detection and analysis of trace components in gases. The approach was to increase the concentration of trace species in the sample flow reaching the analyzer and/or detector. Three methods were explored: (1) <u>Inertial Enrichment</u> in the shock layer of a stagnation sampling probe on the axis of a supersonic free jet of sample gas. (2) <u>Focusing Enrichment</u> in which microdroplets, aerosol particles or heavy molecules comprising or containing analyte species were aerodynamically focused on the centerline of a subsonic free jet at the entrance to a sampling probe. (3) <u>Electrospray Enrichment</u> in which trace species were scavenged by the highly charged small droplets produced by electrospraying an appropriate liquid, then desorbed as ions for analysis by mass spectrometry. Success with (1) was only partial. Thousandfold enrichment of particles could be achieved by (2) and much was learned about the focussing process but chemical analysis aspects were not evaluated. Parts per trillion sensitivity was achieved for several species with (3) which emerged as the most promising approach for future work.							
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified					
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL				

IMPROVEMENT OF GAS ANALYSIS BY ENRICHMENT OF TRACE SPECIES

FINAL REPORT

by

John B. Fenn and Juan Fernandez-de-la-Mora

30 September 1990

U. S. ARMY RESEARCH OFFICE

GRANT DAAL03-87-K-0127

YALE UNIVERSITY  
NEW HAVEN, CT 06520-2159

APPROVED FOR PUBLIC RELEASE

DISTRIBUTION UNLIMITED

90 10 23 056

THE VIEW, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE  
THOSE OF THE AUTHORS AND SHOULD NOT BE CONSTRUED AS AN OFFICIAL  
DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION, UNLESS SO  
DESIGNATED BY OTHER DOCUMENTATION.

## 1. DISCUSSION

A. Statement of the Problem. The objective of this program was to evaluate the possibility of substantially increasing on a continuous basis the concentration of trace constituents in gases in order to increase the effective sensitivity of various kinds of detectors and analyzers for those constituents. Enhancement of sensitivity is always welcome in gas analysis problems such as those involved in the detection, identification and assay of environmental pollutants, drugs, explosives, chemical warfare agents, contaminants in controlled atmospheres and the like.

B. Summary of the Most Important Results. The phenomenon originally contemplated for achieving the desired enrichment was the inertial separation of heavy and light species due to sample deceleration in the stagnation region of a sampling probe inserted in a high speed flow. As the program proceeded, additional variations on the enrichment theme emerged so that this report embodies the results from three separate but related approaches to the problem.

(1) Stagnation Probe Enrichment. Increases in the relative concentration of heavy species occur in sample gas extracted through a stagnation probe on the axis of a small supersonic jet of a gas mixture. Such enrichment was first observed by E. W. Becker and his colleagues. (1) The effect soon found an analytical application in the so-called jet-separator of Ryhage, one of the earliest and most effective interfaces between a gas chromatograph and mass spectrometer in the so-called GC-MS technique that has revolutionized gas analysis. (2) Those early investigators attributed the observed enrichment to pressure-driven radial diffusion that preferentially depleted the light species from the axis of the small supersonic free jet used to provide the high speed flow. Then Reis and Fenn showed that the true explanation of the enrichment was inertial separation during stagnation on the probe tip. (3) Because of their higher mass and greater momentum the heavy species penetrate further into the stagnation zone to achieve increased concentration at the probe face and thus in the gas entering the sampling aperture leading to the analyzer. However, initial perceptions often die hard so that to this day many practitioners of stagnation enrichment, still mistakenly attribute the effect to pressure diffusion.

To use inertial effects for enriching trace components in gas samples we proposed to admit a steady flow of gas to be analyzed through a small orifice into a chamber evacuated by a small mechanical pump. The sampling probe would be placed on the axis of the supersonic jet issuing from the orifice, as in the original experiments of Becker and Ryhage in the mid 1950's. As intuition might suggest, the extent of inertial enrichment depends directly upon the difference in mass (molecular weight) between heavy and light species. It is well known that the adiabatic cooling occurring in the free jet expansion can bring

For ☒  
☐  
☐  
on

ity Codes

Dist

Avail and/or  
Special

A-1

about supersaturation and nucleation-condensation to form clusters or microdroplets of almost any species if the source pressure and specific heat ratio  $C_p/C_v$  of the source gas are high enough and the source temperature is low enough. Clearly, if such clusters or microdroplets comprise or contain the trace analyte species, their much higher masses relative to the carrier gas molecules should result in enhanced enrichment of that species during stagnation. Our idea was to add the vapor of an easily condensable solvent which would act as a "getter" to scavenge the trace species, incorporating them in clusters and microdroplets it (the solvent) formed during the expansion. In this way the effective inertial mass and the resulting enrichment might be increased even for trace species so dilute that they could not achieve homogeneous nucleation, i.e. form pure clusters of themselves. Also to be noted is the fact that such clustering would make possible the enrichment of species whose molecular masses are even lower than those of the carrier gas species. The necessary condition is only that the trace species, alone or in combination with a deliberately added "getter" species, is more readily condensable than the carrier gas. This condition is met for most analytes of interest in atmospheric air.

After some initial problems in restoring to working order an old apparatus equipped with a quadrupole mass analyzer, we carried out an extensive series of experiments in which we did achieve some enhanced enrichment. However, a lot of problems were encountered in adjusting the temperature, pressure and composition of the source gas so that there would be substantial condensation of vapor in the jet but before it entered the nozzle. When such premature condensation occurs the analyte can get "scrubbed" from the gas by the condensate that deposits on the source chamber walls. In addition, the nozzle can become intermittently plugged by condensate. These problems were neither fundamental nor insurmountable but were vexing enough to persuade us that the proportion of effort assigned to this task would be better invested in pursuit of the much more promising results that we had obtained with a new Electrospray technique to be described below in approach (3).

(2) Focusing Enrichment. Investigations by de la Mora and his students before this project began, and continued with its support, showed theoretically that aerosol particles as small as a micron or less could be focused in a subsonic free jet issuing from a simple orifice or converging nozzle. (4) The convergence of streamlines as the fluid flows through the orifice imparts a component of momentum toward the axis of the flow. The result is an "overshoot" of the convergence giving rise to the so called "vena contracta", a slight decrease in the diameter of the jet immediately downstream of the orifice from which it issues. If there is any "slip" of the particles so that their streamlines do not precisely track the fluid streamlines, the particles will converge more than the fluid so that their streamlines will be contained in a stream tube of smaller diameter. The nature and extent of this focusing clearly depends upon the density and

size of the particles, the density and viscosity of the fluid, and the velocity distribution in the flow. In one experiment a dispersion of 0.3 micron polystyrene particles in air was passed through an orifice 0.4 mm in diameter to produce a free jet of Mach number 0.3. At the focal point, 1 mm downstream from the orifice, particle density was 1000 times that in the source gas!

Such remarkable focusing of particles is of great theoretical interest and has strong practical implications for the detection and analysis of dilute aerosols and fumes. It also provided an attractive alternative to inertial enrichment of trace-containing clusters and microdroplets by stagnation of supersonic flow on a stagnation sampling probe as discussed in approach (1) above. Consequently, we spent a fair fraction of our effort in trying to understand and characterize the focusing phenomenon. The three papers that resulted from this work are respectively items (a), (b) and (c) listed in Section C. The following discussion summarizes the important results of each paper, identified here only by the title.

(a) Aerodynamic Focusing of Particles and Molecules in Seeded Supersonic Jets. A review of focusing theory for aerosol particles concludes that: (1) A focal point exists and is infinitely sharp for streamlines near the axis of symmetric nozzles; (2) In spite of a "geometric aberration" that defocuses streamlines far from the axis, numerical calculations show that the width of the focal region may be over 100 times smaller than the nozzle diameter for particles whose initial trajectories are within a moderate solid angle of the jet axis. (3) Focusing occurs only for particles having a Stokes number  $S$  greater than some critical value usually near unity.  $S$  is a dimensionless group that characterizes the un-coupling of fluid and particle velocities. (4) Focusing is sharper when the focal point is within a few nozzle diameters of its exit plane. Experimental data on aerosol particles support these analytical predictions and show focal zone enrichments averaging over 700 for a variety of experimental conditions. Results from some preliminary experiments on ultrafine particles, (large molecules) are also presented and show, as one might expect much less enrichment of the heavy species in the focal zone.

(b) Aerodynamic Focusing of Heavy Molecules in Seeded Supersonic Jets. Results are presented from experiments on focusing of heavy molecules ( $\text{CBr}_4$ ,  $\text{W(CO)}_6$ , and  $\text{C}_2\text{Cl}_4$ ) seeded in jets of helium or hydrogen that are supersonic rather than subsonic as in previous work. A thermcouple probe is developed for determining the radial distribution of heavy species in the jet at various downstream distances from the jet axis. Minimum beam "waists" (focal zone diameters) range from 0.35 to 0.5 of the nozzle diameter. Thus the maximum concentration of seed species is only about 10 times the source gas value compared to factors of 700 or more obtained with aerosol particles.

(c) Brownian-Motion Limited Aerodynamic Focusing of Heavy Molecules. The role of thermal agitation is examined as a possible limiting factor in the aerodynamic focusing of heavy molecules seeded in a light carrier gas. Numerical studies of the problem are carried out by two different methods: hypersonic theory and simulation of Brownian dynamics. A near-axis simplification of the hypersonic equations yields the focusing characteristics of inviscid two-dimensional flows in nozzles with planar walls converging at various angles. The authors conclude it is not possible by aerodynamic focusing of any volatile heavy species to increase concentrations by more than a factor of 10 relative to the source gas. High resolution focusing (enrichment) can be achieved only with mass ratios of tens of thousands, attainable only with microscopic particles several nanometers in diameter or with macromolecules.

(3) Electrospray (ES) Enrichment. Another project in our laboratory involves the development of an electrospray (ES) technique for ionizing non-volatile species including large and complex molecules such as proteins and other biopolymers. (5,6) In ES ionization an analyte solution, e.g. a peptide in methanol-water is electrostatically dispersed as small charged droplets that are driven by an electric field upstream against a counter-current flow of nitrogen bath gas. As the droplets evaporate the combination of increasing charge density and decreasing radius leads to electrostatic fields at the droplet surface that are sufficiently intense to desorb ions from the droplet into the ambient gas. The desorbing ions comprise solute cations or anions to which non ionized solute and/or solvent molecules are attached by ion-dipole forces. Some of these "quasimolecular" ions are entrained in a flow of bath gas that passes through a small orifice into a vacuum system where they are analyzed by a mass spectrometer. In the course of this program we found that several analyte species, added in trace amounts to the bath gas, are apparently absorbed by charged droplets and desorbed as ions that can be "weighed" by a mass analyzer. It has emerged that for some species the scavenging and ionization by ES droplets offers analytical sensitivities much greater than could be achieved with inertial enrichment, whether by stagnation or by focusing.

After some preliminary experiments indicated high sensitivities we assembled a system for producing sample gas with well defined trace concentrations of analyte in a sample gas by injecting dilute solutions of analyte into a heated vaporizer through which a sidestream of sample gas flows and then rejoins the main stream. Injection is by a Liquid-Chromatograph syringe pump that accurately dispenses the analyte solution at a very small flow rate. With this system we were able to detect and identify caffeine, cocaine, RDX and HMX at nominal concentrations as low as 10 to 100 parts per trillion. Only with great pains have mass spectrometers using conventional ion sources achieved equivalent sensitivities. Because of adsorption losses on walls the actual concentrations were probably lower than these nominal values. Moreover, with optimum operating conditions and single

ion monitoring we might be able to detect concentrations lower by another factor of at least 10 or 100. We found that the results depended upon the nature of the solvent and started a systematic study of the solvent role. Unfortunately, our home-made vaporizer broke down. We were then able to borrow one that was developed by the Army and had been used at Extrel but when it arrived its heater was burned out. Shortly after that the grant terminated so we did not obtain any more results with this ES technique for trace analysis in gases. However, we believe that it is very promising new approach and deserves further investigation. The potential applications are manifold.

Frustrated by these hardware problems and interested in producing gaseous dispersions of very large molecules for focusing studies, we investigated the ES ionization of poly (ethyleneglycols) (PEGs), often referred to as poly (ethyleneoxides) (PEOs) when the molecular weight  $M$  is above about 10,000 or so. In previous work we had shown that we could produce intact ions of oligomers of PEG with  $M$  up to 20,000. (7) The results were the first to show the extensive multiple charging of large molecules that ES ionization could achieve and for which it has since become famous. Moreover, in the paper on that work we described a model that predicted an upper limit to the number of charges a PEG oligomer could hold. That limit was characterized in terms of a standoff between the known energy which binds a charge to its site ( $\text{Na}^+$  to an O atom in these experiments) and the electrostatic potential energy due to the pairwise sum of the Coulomb repulsion between the centermost charge and all the others on the oligomer ion. It turned out that  $Z_{\text{obs}}/Z_{\text{mod}}$ , the ratio of observed ion charge to the maximum predicted by the model, decreased from unity (for the monomer) to about 0.5 at  $M = 20,000$ . In the experiments reported here the range of molecular weight for which we could produce intact ions was extended all the way to 5,000,000! We found that at  $M$  greater than 20,000,  $Z_{\text{obs}}/Z_{\text{mod}}$  increased, finally reaching unity at 5,000,000! It is noteworthy that a qualitative explanation of these trends can be based on the idea that desorption from a charged droplet, as proposed by Iribarne and Thomson, is the mechanism by which ES ions are formed from small PEG oligomers. (8) For  $M = 5,000,000$ , it seems clear that an ion is formed by evaporation of solvent from a droplet containing only one macromolecule. This "charged residue" mechanism was the one proposed by Dole in his pioneering experiments. (9) In any case, the ES technique appears to provide a means of invading what has been a no-man's land of gravimetry, the controlled production and weighing of particles with masses between attograms and picograms. Also noteworthy is that each of these largest ions has 4000 or more charges! There is much to think about in terms of the new science and/or technology that these remarkable new species might lead to and the kinds of experiments that should be done with them. The results of this study are reported in a paper identified as (d) in the list of publications in section 3.



### C. List of Publications.

(a) "Aerodynamic Focusing of Particles and Molecules in Seeded Supersonic Jets," J. Fernandez de la Mora, J. Rosell-Llompарт and P. Riesco-Chueca; in Rarefied Gas Dynamics: Physical Phenomena edited by E. P. Muntz, D. P. Weaver and D. H. Campbell, Vol. 117 of Progress in Astronautics and Aeronautics, AIAA, Washington (1989). (Invited paper in the Proceedings of the 18th International Symposium on Rarefied Gas Dynamics, Pasadena 1988)

(b) "Aerodynamic Focusing of Heavy Molecules in Seeded Supersonic Jets," J. Fernandez de la Mora and J. Rosell-Llompарт, Journal of Chemical Physics 91, 2603 (1989).

(c) "Brownian-Motion Limited Aerodynamic Focusing of Heavy Molecules," R. Fernandez-Feria, P. Riesco-Chueca, J. Rosell-Llompарт, J. O'Brien and J. Fernandez de la Mora, Rarefied Gas Dynamics, Proceedings of the 17th International Symposium, (A. E. Beylich, ed.) in press.

(d) "Electrospray Mass Spectrometry of Poly (ethylene glycols) with Molecular Weights up to Five Million," Takashi Nohmi and John B. Fenn, Extended Abstracts of 38th ASMS Conference on Mass Spectrometry and Allied Topics, June, 1990. A manuscript containing a more complete account will be submitted to the Journal of the American Chemical Society.

### D. Participating Scientific Personnel.

#### 1. Principal Investigators:

John B. Fenn, Prof. Emeritus (Chem. Eng.)  
Juan Fernandez de la Mora, Assoc. Prof. (Mech Eng.)

#### 2. Postdoctoral Associates.

Shida Shen (Chem. Eng.)  
Takashi Nohmi (Chem. Eng.)  
Chin Kai Meng (Chem. Eng.)

#### 3. Graduate Student Research Assistants.

P. Riesco-Chueca (Mech Eng. - Ph.D. from Yale)  
Joan D. Rosell-Llompарт (Mech. Eng. - M.S. from University of Barcelona for work at Yale)  
Stephen D. Fuerstenau (Mech. Eng.).

## 2. BIBLIOGRAPHY

1. E. W. Becker, K. Bier, and H. Burghoff, Z. Naturforschung, Teil A 10, 565 (1955)
2. R. Ryhage, Anal. Chem. 36, 759 (1964)
3. V. A. Reis and J. B. Fenn, J. Chem. Phys. 39, 3240 (1963)
4. J. Fernandez de la Mora and P. Riesco-Chueca, J. Fluid Mech. 195, 1 (1988); see also G. W. Israel and S. K. Friedlander, J. Collid Interface Sci. 24, 330 (1967)
5. M. Yamashita and J. B. Fenn, J. Phys. Chem. 88, 4451 (1984); ibid. p 4471.
6. J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong, and C. M. Whitehouse, Science 246, 64 (1989)
7. S. F. Wong, C. K. Meng, J. B. Fenn, J. Phys. Chem. 92, 546 (1988)
8. J. V. Iribarne and B. A. Thomson, J. Chem. Phys. 64, 2287 (1976)
9. M. Dole, L. L. Mach, R. Hines, R. C. Mobley, L. B. Ferguson, M. B. Alice, J. Chem. Phys. 49, 2240 (1968)